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Author(s)	Itoh, Osamu; Kawamura, Takahisa; Ichikawa, Katsuhiko
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1966), 44(3): 207-214
Issue Date	1966-10-31
URL	http://hdl.handle.net/2433/76126
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Chemical and Spectral Behavior of Substituted β-Diketones in Concentrated Sulfuric Acid

Osamu ITOH, Takahisa KAWAMURA and Katsuhiko ICHIKAWA*,**

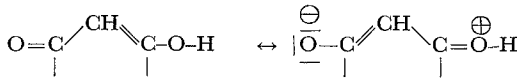
(Ichikawa Laboratory)

(*Received May 31, 1966*)

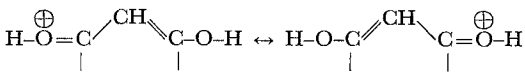
U.v. spectra of substituted β-diketones, including 1,1-diacetylcyclopropanes, have been determined in concentrated sulfuric acid. Four types of spectral change in course of time were observed. I). Absorption maxima of methyl-, ethyl- and *n*-propyl-acetylacetone remained unchanged for three days, and ε_{max} decreased gradually. II). Absorption maximum of isopropylacetylacetone shifted to shorter wave length region with a slight increase of ε_{max} in 20 hrs. After this period, λ_{max} remained unchanged and ε_{max} decreased gradually. III). The spectra of propenyl- and allyl-acetylacetone and 1,1-diacetyl-2-methylcyclopropane were identical even when the measurements were made just after the solutions were prepared, and were identical with those of 3-acetyl-2,5-dimethyl-4,5-dihydrofuran. IV). Absorption maxima of (β-acetoxyethyl)-acetylacetone and 1,1-diacetylcyclporopane shifted to longer wave length region gradually and approached to λ_{max} of 3-acetyl-2-methyl-4,5-dihydrofuran, and only slight decrease of ε_{max} were observed. These spectral changes show a slow deacetylation (type I), de-isopropylation with subsequent decomposition (type II), and fast (type III) and slow dihydrofuran formation (type IV) respectively.

Many papers have been published on the ultraviolet absorption spectra of β-diketones concerning their keto-enol equilibria[1]. Recently Yoffe and co-workers reported the u. v. spectra of α-substituted β-diketones in organic solvents[2]. In a previous paper, the present authors also reported those of the β-diketones substituted with chloromercuri-alkyls and -aralkyls and of the non-enolizable β-diketones including 1,1-diacylcyclopropanes as the special case[3]. As a part of the study on the basicity of β-diketone, Eistert and co-workers reported that λ_{max} of oxonium ions which were formed from β-diketones by protonation in concentrated sulfuric acid shifted to longer wave lengths as compared with those of unprotonated enols in organic solvents. This is because of the lower excitation energy due to the more symmetrical resonace hybrid forms of the oxonium ions than those of the corresponding enols[4].

Enol:



Enol oxonium cation:



In order to investigate the effects of strong acid on the the absorption spectra and chemical behavior of α-substituted β-diketones including 1,1-diacetylcyclopropanes, u. v. spectra of these compounds have been determined in concentrated sulfuric acid.

All of the discussion described below is concerned with the oxonium ions formed by protonation on carbonyl oxygen, if not mentioned otherwise, because β-diketones

* 伊藤修．河村隆久．市川克彦

** Inquiries and reprint requests should be addressed to K.I.

in concentrated sulfuric acid exist in this form according to Eistert's conclusion.

U. v. spectra of most of the β-diketones studied here changed in both λ_{max} and ε_{max} in course of time after the sulfuric acid solutions were prepared for the spectral measurements. Four types of spectral change were observed.

Type I. Values of λ_{max} of methyl- (**II**), ethyl- (**III**) and *n*-propyl-acetylacetone (**IV**) remained unchanged even after 60 hrs., and ε_{max} decreased gradually.

Type II. In the case of isopropyl-acetylacetone (**V**), λ_{max} (307 mμ) shifted to a shorter wave length (288 mμ) after 20 hrs., while ε_{max} incresed slightly. After this period, λ_{max} remained unchanged and ε_{max} decreased gradually. The value of λ_{max} 288 mμ is the same with that of acetylacetone.

Type III. The spectra of propenyl- (**IX**), allyl-acetylacetone (**X**) and 1,1-diacetyl-2-methylcyclopropane (**XII**) showed absorption maxima at the same wave lengh of 312 mμ. As is mentioned later, these λ_{max} cannot be assigned to those of the starting compounds. It seems likely that these diketones form a same product in sulfuric acid rapidly.

Type IV. The spectra of (β-acetoxyethyl)-acetylacetone (**VIII**) and 1,1-diacetylcyclopropane (**XI**) changed gradually in both λ_{max} and ε_{max}, and approached to those of 3-acetyl-2-methyl-4,5-dihydrofuran.

Data obtained are listed in Table 1.

Table 1. U. v. absorption spectra of substituted β-diketones and dihydrofurans in concentrated sulfuric acid.

Time[a]	5–8 min.		20 hrs.		40–50 hrs.		60 hrs.	
Compound	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
I	288	4.18						
II	306	4.10						
III	307	4.15	307	3.83	307	3.55		
IV	308	4.18						
V	307	3.64	288	3.75	288	3.64	288	3.38
VI	303	3.06			303	1.54		
	85% acid							
	305	3.16	305	3.15	305	3.15		
	65% acid							
	305	2.86	305	2.71			305	2.49
	55% acid							
	303	2.40	303	2.24			303	1.90
VII	252	3.92						
	298	3.52						
VIII	297	4.16	308	4.10			312	4.08
IX	313	4.16						
X	313	4.20						
XI	299	4.25	303	4.19	309	4.10	313	4.06
XII	313	4.13					(150 hrs.)	
XIII	312	4.13						
XIV	311	4.19						

Table 1. (continued)

I. $CH_3COCH_2COCH_3$,

II. $CH_3COCH(CH_3)COCH_3$,

III. $CH_3COCH(CH_2CH_3)COCH_3$

IV. $CH_3COCH(CH_2CH_2CH_3)COCH_3$,

V. $CH_3COCH(CH_3CHCH_3)COCH_3$,

VI. $CH_3CO(C(CH_3)_2)COCH_3$

VII. $CH_3CO(C(=CHCH_3))COCH_3$,

VIII. $CH_3COCH(CH_2CH_2OAc)COCH_3$,

IX. $CH_3COCH(CH=CHCH_3)COCH_3$

X. $CH_3COCH(CH_2CH=CH_2)COCH_3$,

XI. $CH_3CO(C(CH_2-CH_2))COCH_3$,

XII. $CH_3CO(C(CH_2-CHCH_3))COCH_3$

XIII. $H_2C(-CCOCH_3)(-CCH_3)(-O-)$,

XIV. $H_2C(-CCOCH_3)(-CH(CH_3)-CCH_3)(-O-)$

a) Time interval between the preparation of the solution and the spectral mesaurement.

The spectral behavior of type I is similar to that of unsubstituted acetylacetone reported by Eistert. This appears to show the destruction of β-diketo skeleton, probably by deacetylation. An example of time-spectra relation is shown in fig. 1. Since preparative experiments showed that these compounds could be recovered from the solutions in fairly good yields, the spectra of earlier measurements can be assigned to those of the β-diketones.

The change of the spectra of **V** (type II, shown in fig. 2) makes a sharp contrast to that of type I. The shift of λ_{max} to 288 mμ with a slight increase of ε_{max} shows a conversion to a product without losing β-diketo skeleton. Since acetylacetone is the only possible β-diketone which shows absroption maximum at 288 mμ, it can be concluded that dealkylation of **V** to form acetylacetone proceeds first, and then the decompostion of β-diketone follows. Since the more facile splitting of isopropyl group than normal alkyl groups is recognized widely in aromatic dompounds, there is no reason why the same tendency cannot be expected in the case of substituted β-diketones.

The spectra of **IX**, **X** and **XII** were identical even when the measurements were made as soon as the solutions were prepared, and it seems likely that these three compounds react rapidly to form the same compound in sulfuric acid. Preparative experiments proved that this is the case. When the sulfuric acid solutions of these compounds were diluted with water half an hour after preparing the solution, and extracted with ether, 3-acetyl-2,5-dimethyl-4,5-dihydrofuran (**XIV**) was obtained in all cases. It is clear that **IX**, **X** and **XII** form **XIV** rapidly in concentrated sulfuric acid and the spectra observed are those of **XIV**. This was reconfirmed by the fact that the spectra of **XIV** which was separated and redissloved were identical with those of **IX**, **X** and **XII** in both λ_{max} and ε_{max}. It appears that **XIV** is formed from **IX** and **X** through protonation to the double bonds leading to a common secondary carbonium ion and subsequent intramolecular O-alkylation. **XII** appears to form the the same carbonium ion by ring opening.

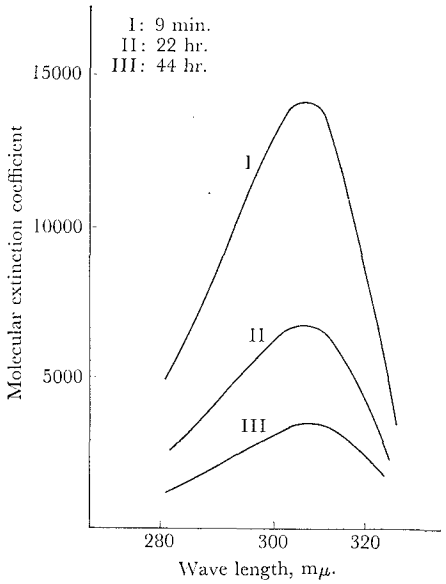


Fig. 1. U. v. spectrs of ethylacetylacetone in sulfuric acid.

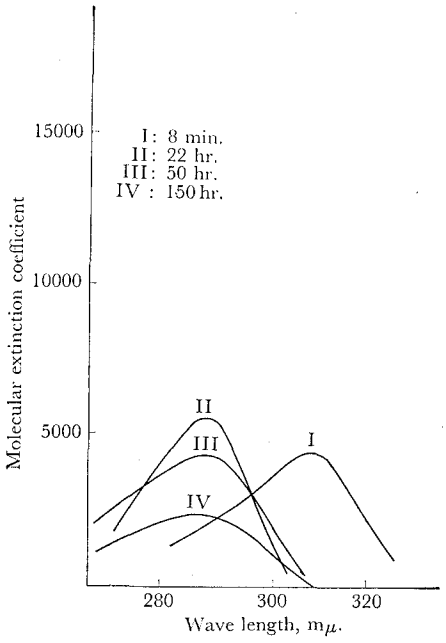


Fig. 2. U. v. spectra of isopropylacetylacetone in sulfuric acid.

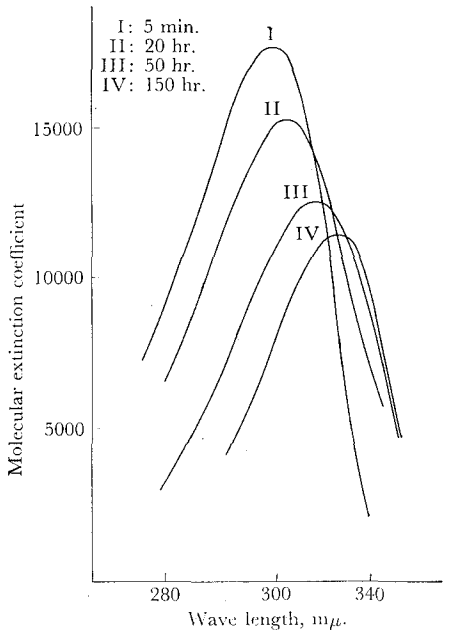
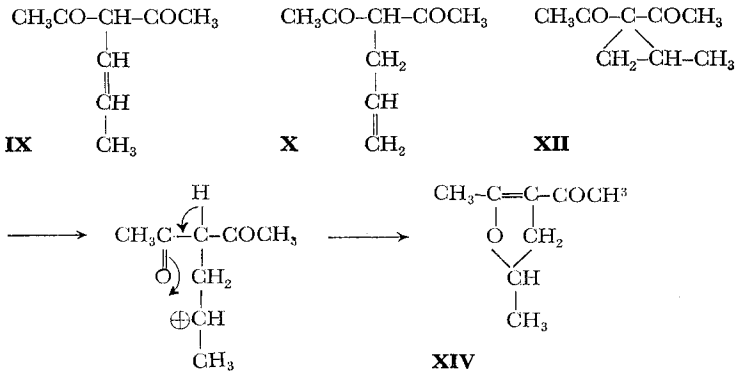
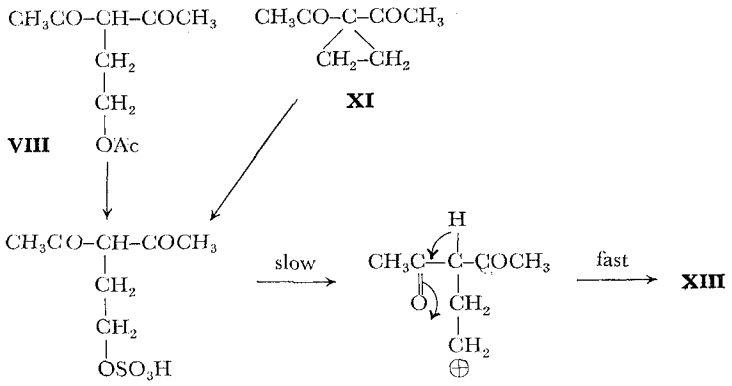


Fig. 3. U. V. spectra of 1,1-diacetylcyclopropane in sulfuric acid.



Sulfuric acid solutions of **VIII** and **XI** gave 3-acetyl-2-methyl-4,5-dihydrofuran (**XIII**), when diluted with water and extracted with ether, as in the case mentioned above. On the other hand, the spectra of **VIII** and **XI** in the earlier stage of the measurement apparently differed from those of **XIII**. This phenomenon can be explained by the following mechanism. The compounds, **VIII** and **XI** react first to



form the common sulfate, from which carbonium ion is formed and gives **XIII**. In contrast to the case of the formation of **XIV**, the intermediate carbonium ion is primary and its formation is much slower than that of secondary one. Therefore, the rate of formation of **XIII** is much slower and this reflects to the slow spectral change. The spectra observed in the early stage of the measurements can be assigned to those of the sulfate. In the case of preparative experiments, the concentrations are much higher than those of spectral measurements, and it is not surprising that the dihydrofuran was obtained at only 30 minutes after the compounds were dissolved in sulfuric acid.

Dimethyl-acetylacetone (**VI**) is a non-enolizable β-diketone. Therefore, the absorption observed at 292 mμ in hexane[3] is not due to $\pi \rightarrow \pi^*$ transition as in the cases of other β-diketones, but to $n \rightarrow \pi^*$ transition of carbonyl group. Since this transition is "prohibited" one, the value of $\log \varepsilon = 2.43$ is unusually large. The same phenomena were observed in sulfuric acid solutions, and the higher the concentration of sulfuric acid was, the larger the value of $\log \varepsilon$ was. The reason of these

results is not easy to explain and will be studied in future.

The spectral change of **VI** belongs to type I. The rate of decrease of ε was the fastest in 95% acid. When the acid concentration was 85%, the rate was the slowest. This suggests that two different mechanisms of the decomposition of **VI** are operative in the concentration ranges of higher and lower than 85% respectively.

Ethylidene-acetylacetone (**VII**) showed two absorption maxima which might be be due to cis- and trans-α,β-unsaturated carbonyl group. Definite assignment, however, requires further investigation.

From the results mentioned above, it is clear that careful consideration is required to discuss the u.v. spectra of β-diketones in sulfuric acid. For example, the spectra which were obtained with **IX**, **X** and **XII** do not tell anything about the spectra of these diketones themselves. In the cases of **I**, **II**, **III**, **IV**, **V** and **VI**, the spectra obtained are those of the oxonium ions which are formed by protonation on oxygen of carbonyl, if data of early stage of measurements are used. Concerning the effects of alkyl-substituent on the spectra, it can be concluded that alkyl substitutions at α-carbon of acetylacetone shift the absorption maximum to longer wave length region by 19 ± 1 mμ. The shifts were independent of the structure of the alkyl group in **I**–**V**.

Finally, it must be mentioned on the descrepancy between the spectral data of isopropylacetylacetone by Yoffe and co-workers and by ourselves. In hexane solution, Yoffe gave $\lambda_{max}=251$ mμ and $\varepsilon=3600$. According to our experiments, λ_{max} and ε were 298 mμ and 244 respectively. Yoffe's data show that appreciable amount of enol form must exist in hexane solution. Our careful examination by infrared spectroscopy and by n. m. r. in deuteriochloroform solution could not detect the presence of enol form. We believe that our data are correct.

EXPERIMENTAL

Material. Commercial sulfuric acid (analytical grade, 95%) was used for the

Table 2. β-Diketones used for u. v. spectra measurement.

	Boiling point, °C/mmHg		Refractive index (20°)	
		reported		reported
II	75– 78/26	86/ 60[1]	1.4421	1.4420[1]
III	80– 82/20	83– 85/35[1]		1.4415[1]
IV	93– 95/25	87– 89/17[1]		1.4463[1]
V	77– 80/19	82– 83/20[1]		1.4420[1]
VI	79/27	54/8[1]	1.4299	1.4311[1]
VII	100–112/22	44– 45/0.04[2]		1.4608 (25°)[2]
VIII	113–115/ 5	107–108/ 2.5[3]	1.4597	
IX	82– 90/16	82/14[4]		1.4875 (25°)[4]
X	190–225	195–196[5]		

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experiments. Acetylacetone was also a commercial product and used after careful distillation. Substituted β-diketones, **II**, **III**, **VI**, **VII**, **VIII**, **IX** and **X** were prepared by the methods that were reported in the literature and listed in table 2. By hydrogenation of **IX** with platinumblack catalyst, **IV** was prepared. The preparation of **V** (borohydride reduction of 3,3-diacetyl-2-methyl-propylmercuric chloride), **XI** and **XII** was reported in a previous paper. By gas-chromatography, it was confirmed that all these samples except **VII** contained no detectable amounts of inpurities. Despite careful distillations, **VII** contained unknown impurity of less than 2%.

Spectral measurement. According to usual method, spectra were determined by HITACHI EPS-2U.

Recovery of β-diketones from sulfuric acid solution. The experimental procedure is the same as that of isolation of **XIII** that is described below. The yields of recovery were 50, 60, 60 and 20% in the cases of **I**, **IV**, **VI** and **VIII** respectively. By gaschromatography, it was confirmed that the recovered ones were the same with the original samples.

3-Acetyl-2-methyl-4,5-dihydrofuran (XIII). 1,1-Diacetyl-cyclopropane (5.0 g.) was dissolved into 20 ml. of sulfuric acid (commercial, analytical grade, 95%). After standing for half an hour, the solution was added with 100 ml. of water, and extracted with 70 ml. of ether five times and then with 70 ml. of benzene three times. The ether- and benzene-extracts were combined together respectively and washed with aqueous saturated sodium bicarbonate. The water layer was neutralized with dilute aqueous sodium hydroxide solution and then extracted with 70 ml. of ether five times and then with 70 ml. of benzene three times. The ether and benzene extracts were combined together respectively and dried with sodium slufate. Distillation of the ether extract gave 3.0 g. (b.p.~103°/25 mm Hg) and the benzene extract 0.8 g. (b.p.~110°/35 mm Hg) of liquid respectively. Comparing with the authentic sample[6] these liquid products were shown to be **XIII** with unknown impurity of about 2%, by gas-chromatography and infrared absorption. The yield was 78%.

3-Acetyl-2,5-dimethyl-4,5-dihydrofuran (XIV). The solution of **XII** (1.7 g.) in 95% sulfuric acid (7 ml.) was worked up as in the case of **XI**. A quantity of 1.2 g. of **XIV** (b.p. ~95°/13 mm Hg, 70% yield) was obtained. U.v. and i.r. spectra of this liquid showed the presence of 3-acetyl-2-methyl-dihydrofuran skeleton. The n.m.r. spectra showed signals at τ 8.62 (doublet), 7.79 (singlet+triplet), 7.67–6.67 (multiplet) and 5.0–4.6 (multiplet) with relative intensities of 3:6:2:1, which can be assigned to protons of 5-methyl, 3-acetyl+2-methyl, methylene (4) and methine (5) respectively.

From sulfuric acid solutions of **IX**, and **X**, the same product was obtained with 34 and 35% yield respectively.

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